

Alternant Conjugate Systems. III. Syntheses of Stereoisomeric *p, p'*-Distyrylstilbenes and Related Compounds

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(Received March 7, 1961)

In Part II¹⁾ of this series, the present authors reported the syntheses of alternatively conjugated compounds containing three benzene rings in the conjugate system. The appearance of absorption maxima at ca. 270 m μ in the ultraviolet spectra of these compounds could be attributed either to the so-called "cis-peak"²⁾ or to the partial chromophore³⁾ which became operative at the presence of steric hindrance. As it seems to be possible to distinguish the two possibilities stated above by an examination of the ultraviolet spectra of the longer alternant conjugate system, the authors have carried out the syntheses of stereoisomeric *p, p'*-distyrylstilbenes and the related compounds containing four benzene nuclei in the system.

Theoretically, eighteen stereoisomers are possible in the alternant conjugate system containing four benzene nuclei which are linked with each other by double or triple bonds in their para-positions. The present paper deals with the syntheses of ten of the eighteen stereoisomers of this series.

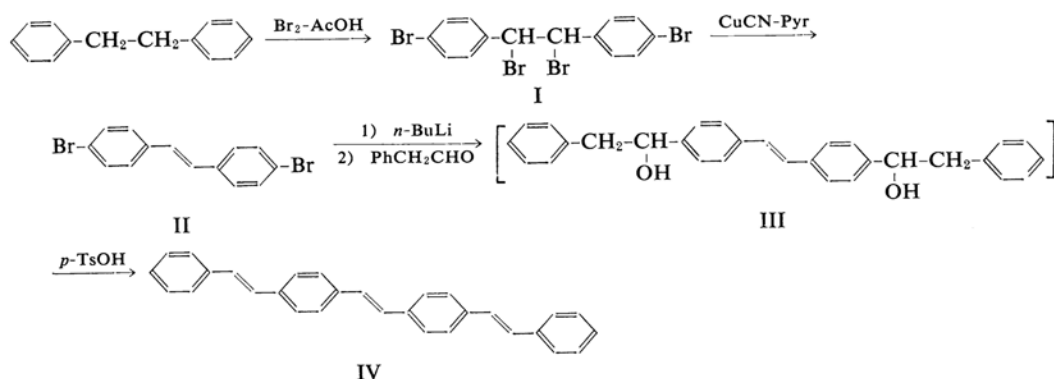
The all-trans isomer has been synthesized by Dale⁴⁾ through the Meerwein reaction of *p, p'*-diaminostilbene and by Drefahl and his co-worker⁵⁾ through the Grignard reaction of *p, p'*-stilbenedialdehyde. The present authors

have synthesized the all-trans isomer according to the following scheme⁶⁾.

p, p'-Dibromostilbene (II) was derived from the tetrabromide (I) by treatment with cuprous cyanide⁷⁾. The crude glycol (III) which was obtained by the metalation of the stilbene (II) and the subsequent reaction with phenylacetaldehyde was dehydrated without further purification, yielding trans, trans, trans-*p, p'*-distyrylstilbene (IV) as yellow crystals with green fluorescence.

Two different methods, a half-reduction of the corresponding acetylenic analogues and the Wittig reaction of the appropriate aldehyde with a phosphonium halide, were employed for the syntheses of trans, cis, trans- and trans, trans, cis-isomers of *p, p'*-distyrylstilbene (abbreviated as t-c-t and t-t-c).

The t-c-t isomer was synthesized according to the following scheme: *p, p'*-Dibromotolan (V) was obtained in an almost quantitative yield by the dehydrobromination⁸⁾ of the tetrabromide (I). Successive reactions of *n*-butyllithium with dibromotolan (V) and then with phenylacetaldehyde yielded the glycol (VI). The glycol (V) was dehydrated in boiling toluene in the presence of *p*-toluenesulfonic acid to yield trans, trans-*p, p'*-distyryltolan



1) Part II: S. Misumi, M. Kuwana, K. Murashima and M. Nakagawa, *This Bulletin*, **34**, 1833 (1961).

2) L. Zechmeister, L. Pauling et al., *J. Am. Chem. Soc.*, **65**, 1940 (1943); L. Zechmeister, *Chem. Revs.*, **34**, 267 (1944); *Experientia*, **10**, 1 (1954).

3) W. Oroshnik and A. D. Mebane, *J. Am. Chem. Soc.*, **76**, 5719 (1954). cf. P. Karrer et al., *Helv. Chim. Acta*, **35**, 1850 (1952); **36**, 562 (1953).

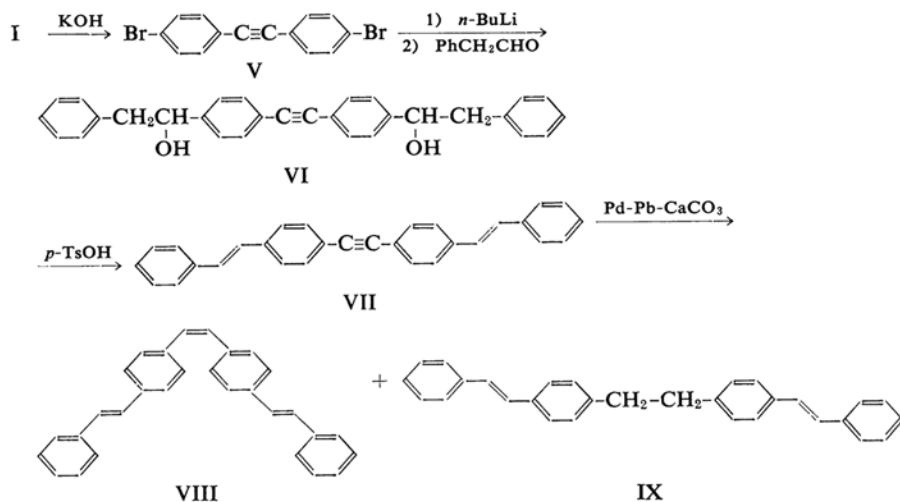
4) J. Dale, *Acta Chem. Scand.*, **11**, 971 (1957).

5) G. Drefahl and G. Plötnner, *Chem. Ber.*, **91**, 1274 (1958).

6) S. Misumi and M. Kuwana, presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

7) S. Bance, H. J. Barker and A. M. Woolman, *J. Chem. Soc.*, **1943**, 1.

8) H. J. Barker and R. Slack, *ibid.*, **1944**, 612.



(VII)⁶⁾ (abbreviated as t-A-t).

t-A-t (VII) was found to be sparingly soluble in common solvents for catalytic hydrogenation. Therefore, VII was dissolved in a large amount of tetrahydrofuran (solubility: 3 mg. in 43 ml.) and hydrogenated in a dark place over a large amount of Lindlar's catalyst⁹⁾ (about the same weight as VII). The progress of hydrogenation was followed, measuring the change of the ultraviolet absorption at a certain time interval. The hydrogenation product from several runs was combined (300 mg.) and recrystallized from benzene. This substance yielded almost pure t-c-t isomer by chromatographic purification over alumina. The configuration of this material was inferred from the following evidence: (1) Analytical data, (2) definite and sharp melting point, (3) thermal isomerization to all-trans isomer, and (4) photoisomerization to all-trans isomer.

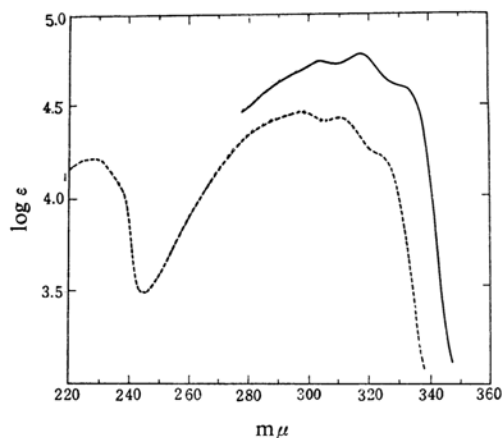
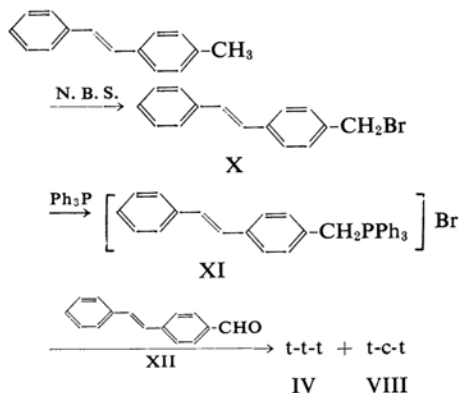


Fig. 1. The ultraviolet spectra of IX (—) (in benzene) and *p*-methylstilbene (.....) (in *n*-hexane).

Pale yellow needles with green fluorescence (m. p. 262°C.) were obtained from the first mother liquor of the recrystallization of t-c-t isomer. The solubility in organic solvents and the closely related ultraviolet spectrum of this compound with that of *p*-methylstilbene (maxima at almost the same positions with two-fold intensities) suggest that the substance with the melting point of 262°C is *p*,*p'*-di-styryldibenzyl (IX) (Fig. 1 and Table I).

The t-t-t and t-c-t isomers were also prepared by the Wittig reaction. The reaction of the phosphonium salt XI, derived quantitatively from *p*-bromomethylstilbene (X), with *p*-stilbenealdehyde (XII)¹⁰⁾ resulted in a mixture of



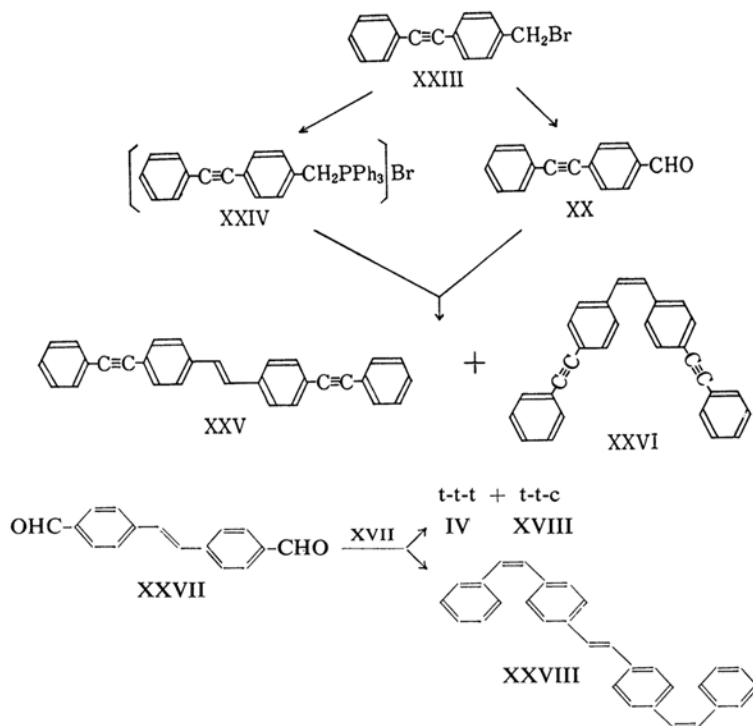
t-t-t (IV) and t-c-t isomer VIII. Recrystallization and chromatography over alumina of the mixture afforded pure t-t-t and t-c-t isomer.

The synthesis of the third isomer, t-t-c (XVIII), was performed starting from *p*-tolualdehyde (XIII)¹¹⁾. *p*-Methyldistyrylbenzene (XIV)⁵⁾ was prepared by the Wittig reaction

10) Part I: S. Misumi, This Bulletin, 34, 1827 (1961).

11) G. H. Coleman and D. Craig, "Organic Syntheses", Col. Vol. II, 583 (1943).

9) H. Lindlar, *Helv. Chim. Acta*, 35, 446 (1952).



which was prepared by the above-mentioned Wittig reaction, by the mixed melting point determination and by a comparison of the ultraviolet spectra.

With the purpose of comparing the ultraviolet spectroscopic properties with those of analogous alternant triene or alternant dienyne compounds, *cis*- and *trans*-*p,p'*-bisphenylethynylstilbenes (XXVI, A-c-A and XXV, A-t-A¹²⁾) were synthesized by the reaction of phosphonium salt XXIV with tolanaldehyde (XX), both of which are derived from *p*-bromomethyltolan (XXIII). The structure of the *cis*-isomer was determined by the analytical data and the thermal- and photo-isomerizations to the A-t-A isomer.

The fourth isomer of *p,p'*-distyrylstilbene, c-t-c (XXVIII), was obtained by a double Wittig reaction of *p,p'*-stilbenedialdehyde (XXVII) together with t-t-t (IV) and t-t-c (XVIII). The structure of this isomer was confirmed by elementary analysis and the thermal- and photo-isomerizations to the t-t-t isomer. It is interesting to note that this isomer is thermally more stable than t-t-c (VIII) and t-t-c (XVIII).

Generally, a slightly larger or almost the same amount of *cis*-isomer as compared with that of *trans*-isomer could be isolated from the products of the Wittig reactions of these types of compound. This fact seems to be attributable to the difficult isolation and

purification of the sparingly soluble *trans*-isomer from the unreacted phosphonium salt in contrast with the case of the more soluble *cis*-isomer.

The ultraviolet spectra of the above-mentioned ten compounds, t-t-t, t-t-c, t-c-t, c-t-c, t-t-A, t-A-t, A-t-A, A-c-A, t-c-A and A-A-A, are illustrated in Figs. 2, 3 and 4. The physical properties of these compounds are presented in Table II. A detailed discussion on the ultraviolet spectra and the photoisomerizations of these compounds will be presented in a following paper.

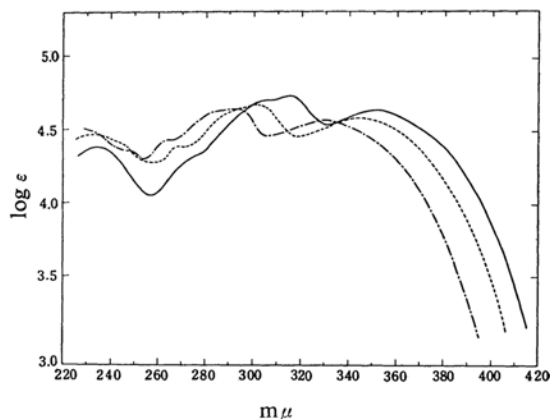


Fig. 2. The ultraviolet spectra of t-t-t (VIII, —), t-c-A (XXII,), and A-c-A (XXVI, —·—·) in tetrahydrofuran.

TABLE II. PROPERTIES OF STEREOISOMERIC *p,p'*-DISTYRYLSTILBENES AND RELATED COMPOUNDS

	M. p., °C	Color	Fluorescence in solution	Ultraviolet spectrum λ_{\max} in $m\mu$ ($\epsilon_{\max} \times 10^{-3}$) in tetrahydrofuran		
t-t-t	334~336	Green yellow	Intense blueviolet	238 (35.9)	270 (18.6)	384 (89.3)
t-t-A	308~309	Light green yellow	Intense blueviolet	237 (32.1)	266 (20.8)	374 (78.7)
t-A-t	305~308	Light green yellow	Intense blueviolet	243 (43.2)		361 (84.3)
A-t-A	278~279	Light green yellow	Blueviolet	235 (29.7)	262 (14.4)	362 (80.1)
t-t-c	227~230	Light green yellow	Blueviolet	237 (28.5)		372 (68.1)
t-c-t	227~228	Light yellow	Light greenblue	236 (22.9)	316 (52.1)	353 (41.0)
c-t-c	111~112	Pale yellow	Colorless	238 (36.8)		359 (48.8)
t-c-A	198~199	Light yellow	Colorless	235 (29.0)	270 (24.1)	302 (45.7)
A-c-A	151~152	Colorless	Colorless		295 (45.3)	330 (36.5)

c, t and A denote *cis*-ethylenic, *trans*-ethylenic and acetylenic linkage respectively.

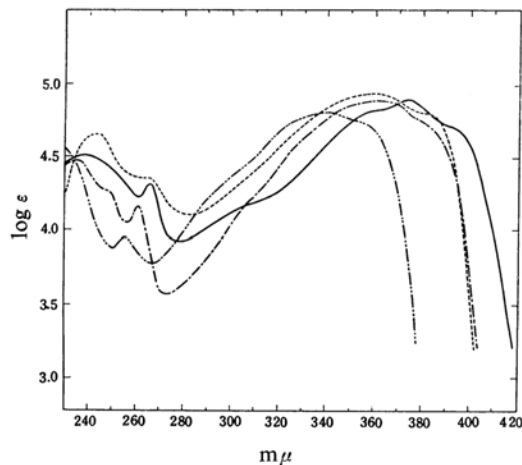


Fig. 3. The ultraviolet spectra of t-t-A (XXI, —), t-A-t (VII,), A-t-A (XXV — · — ·) (in tetrahydrofuran) and A-A-A (— · — ·) (in chloroform).

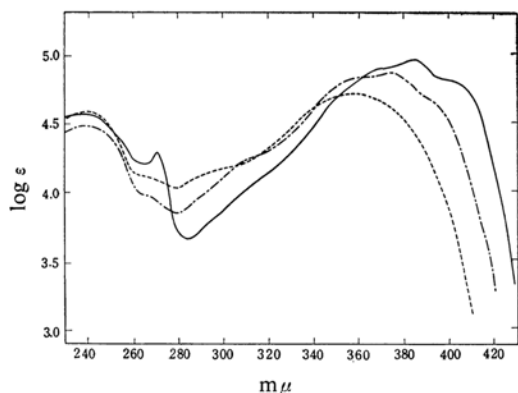


Fig. 4. The ultraviolet spectra of *p,p'*-distyrylstilbenes (t-t-t, IV, —; t-t-c, XVIII, — · — ·; c-t-c, XXVIII,), in tetrahydrofuran.

Experimental*

***trans, trans, trans-p, p'*-Distyrylstilbene (t-t-t) (IV).** — *a*) From *p, p'*-Dibromostilbene (II). — The debromination of *p, p', α, α'*-tetrabromodibenzyl (I) according to the method of Bance et al. yielded *p, p'*-dibromostilbene (II), in the form of lustrous colorless plates, m. p. 207.5~209°C (81.7%) (lit., m. p. 206~210°C, 72%)²¹. A small excess of *n*-butyllithium in dry ether was slowly stirred into a suspension of dibromostilbene (II, 16.6 g., 0.049 mol.) in dry ether (170 ml.) in an atmosphere of pure nitrogen. The reaction mixture was kept overnight at room temperature, and then freshly distilled phenylacetaldehyde (15.0 g., 0.125 mol.) in dry ether (170 ml.) was slowly stirred into the mixture over a period of 1 hr. The stirring was continued for a further 10 hr., and then the mixture was refluxed for 4 hr. A slow stream of pure nitrogen was introduced continuously into the reaction flask throughout these operations. A saturated aqueous solution of ammonium chloride (10.7 g.) was added to the cooled reaction mixture. The crystals accumulated on the intersurface of organic and aqueous layers were collected by filtration (16.4 g.). The aqueous layer was extracted with ether. The extract was combined with the ethereal layer and washed with water. The solvent was removed from the dried ethereal solution, yielding crude glycol III (19.4 g.). The crude material was combined (35.8 g.) and dissolved in toluene (450 ml.). The toluene solution was refluxed for 7 hr. in the presence of a small amount of *p*-toluenesulfonic acid, and the water formed was removed continuously by means of a water-separator. Deposition of yellow crystals was observed during the course of dehydration. The mixture was cooled, and the crystals deposited were filtered. The crude crystals were recrystallized from chlorobenzene to give IV, on greenish yellow plates, m. p. 295~305°C,

* All melting points were measured on a Kofler block and were not corrected.

6.7 g. (35.6%). This material was recrystallized twice from the same solvent to yield pure IV, m. p. 334~336°C.

Found: C, 93.38; H, 5.99. Calcd. for $C_{30}H_{24}$: C, 93.71; H, 6.29%.

b) *By the Wittig Reaction.*—IV was also obtained as a by-product of the syntheses of *trans, cis, trans, trans, cis, cis, trans, cis-p, p'*-distyrylstilbenes according to the Wittig reaction. The experimental details will be described in section b) on the syntheses of VIII and XVIII and the synthesis of XXVIII.

***trans, trans-p, p'*-Distyryltolan (t-A-t) (VII).**—*p, p'*-Dibromotolan (V).—Finely powdered tetrabromide (I, 40 g., 0.08 mol.) was added to a solution of sodium ethoxide in absolute ethanol (sodium, 38 g., 1.65 mol. in absolute ethanol, 600 ml.), and the mixture was refluxed for 1 hr. The reaction mixture was poured into water (1.5 l.) and the precipitate formed filtered. The dried precipitate was recrystallized from chloroform to yield dibromotolan (V), on lustrous plates, m. p. 182~183°C, 25.6 g. (95.2%) (lit., m. p. 182~184°C, 74%¹³). Further recrystallization gave the analytically pure sample, m. p. 184.5~185°C.

Found: Br, 47.84. Calcd. for $C_{14}H_8Br_2$: Br, 47.57%.

p, p'-Bis(α -hydroxy- β -phenylethyl)tolan (VI).—The glycol (VI) was obtained through the metalation of the dibromotolan (V, 13.5 g., 0.04 mol.) and the subsequent reaction with phenylacetaldehyde (11.5 g., 0.096 mol.) as for the synthesis of t-t-t (IV). The crude glycol (20.7 g.) was twice recrystallized from benzene-light petroleum (1:3) to give pure VI, in the form of colorless fine crystals, m. p. 155.5~157.5°C, 4.6 g. (27.2%).

Found: C, 85.90; H, 6.32. Calcd. for $C_{30}H_{26}O_2$: C, 86.09; H, 6.26%.

IR_{max} (cm⁻¹) 3350 (ν OH), 1052 (δ OH).

***t-A-t* (VII).**—A solution of the acetylenic glycol (VI, 2.5 g.) and *p*-toluenesulfonic acid (1.0 g.) in dry toluene (150 ml.) was refluxed for 2 hr., with a continuous removal of water. The crystals separated on cooling were filtered and recrystallized twice from chlorobenzene, yielding VII, in the form of pale greenish yellow leaflets, m. p. 305~308°C, 1.6 g. (70%).

Found: C, 94.19; H, 5.72. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80%.

***trans, cis, trans-p, p'*-Distyrylstilbene (t-c-t) (VIII).**—a) *From t-A-t (VII) by Partial Reduction.*

—t-A-t (VII) in a large amount of tetrahydrofuran was hydrogenated over Lindlar's catalyst (about the same amount as VII) by shaking a dark brown flask in a dark place. The progress of hydrogenation was followed by measuring the change of the ultraviolet spectrum at 30 min. intervals instead of by observing the change of the absorption curve of hydrogen. It required about 2.5 hr. to complete the half-reduction. The reduction products from several runs were combined (ca. 300 mg.) and digested with hot benzene. The hot solution was filtered to remove the insoluble material (a mixture of t-A-t and t-t-t). Pale yellow crystals, m. p. 210~220°C, were obtained on cooling the filtrate. The crystals were dissolved in benzene and chromatographed on alumina in a dark place. The column

was eluted first with benzene, then with benzene-alcohol and finally with alcohol. Fractions 1 and 2, eluted with benzene gave crystals of m. p. 225~227°C, whereas fractions 3~6, eluted with benzene, gave crystals of m. p. 261~262°C. Fraction 8, eluted with benzene-alcohol, furnished crystals of m. p. ca. 300°C. (sublime). The crystals obtained from the fractions 1 and 2 were recrystallized from benzene, resulting in t-c-t (VIII), in the form of pale yellow plates with a pale green fluorescence, m. p. 227~228°C.

Found: C, 93.50; H, 6.30. Calcd. for $C_{30}H_{24}$: C, 93.71; H, 6.29%.

Resolidification was observed when VIII was kept in a molten state for several minutes. The resolidified material began to sublime near 300°C and melted ca. 320°C, indicating the thermal isomerization to all-trans isomer (m. p. 334~336°C). Also an identical ultraviolet absorption curve with that of t-t-t isomer was obtained after the insolation of a solution of VIII in *n*-hexane.

The crystals obtained from fractions 3~6 were recrystallized from chlorobenzene, yielding IX, in the form of pale yellow needles, m. p. 262°C. An analysis could not be performed, however, because of the small amount.

b) *From p-Stilbenealdehyde by the Wittig Reaction.*

—*p*-Styrylbenzyltriphenylphosphonium Bromide (XI).—A mixture of *p*-methylstilbene (15 g., 0.077 mol.), *N*-bromosuccinimide (15 g., 0.084 mol.)¹³ and benzoyl peroxide (200 mg.) in carbon tetrachloride (150 ml.) was stirred for 8 hr. under reflux. The cooled reaction mixture was filtered to remove the succinimide. The imide was washed repeatedly with carbon tetrachloride. The combined filtrate and washing were concentrated under reduced pressure. The crystals thus obtained were washed with ethanol, resulting in colorless crystals, m. p. 119~121°C, 12.5 g. (57%). Finely powdered triphenylphosphine (20 g., 0.076 mol.) was added to a solution of the crude bromide (8 g., 0.029 mol.) in xylene (150 ml.), and the mixture was stirred for 4 hr. with gentle refluxing. The crystals deposited on cooling the reaction mixture were filtered and washed with ethanol, resulting in phosphonium bromide, XI, in the form of colorless fine needles, m. p. 286~288°C, 14.5 g. (92%).

***trans, cis, trans-p, p'*-Distyrylstilbene (t-c-t) (VIII) and *trans, trans, trans-p, p'*-Distyrylstilbene (t-t-t) (IV).**

—To a stirred suspension of *p*-stilbenealdehyde (XII, 2.0 g., 9.6 mmol.) and the phosphonium bromide (XI, 6.0 g., 11.2 mmol.) in absolute ethanol (120 ml.) was added a solution of lithium ethoxide in absolute ethanol (from 0.15 g. of lithium and 70 ml. of absolute ethanol). Fine yellow crystals were gradually deposited as the phosphonium salt disappeared. The crystals were filtered without suction and digested with hot benzene. The insoluble portion was recrystallized from chlorobenzene, yielding t-t-t isomer, IV, in the form of greenish yellow plates, m. p. 328~330°C, 0.08 g. A melting point depression was not observed on admixture with the authentic t-t-t isomer.

The benzene soluble portion was chromatographed

13) Y. Yukawa and U. Suzuki, *Mem. Inst. of Sci. Ind. Research, Osaka*, 10, 190 (1952).

over alumina in a dark place, and the column was eluted with benzene. The column was exposed occasionally to ultraviolet light for a short time, and the shift of the absorption band was located by observing the fluorescence which is characteristic of the t-c-t isomer. Fractions 1 and 2, eluted with benzene, afforded VIII, in the form of light yellow plates, m. p. 227~228°C. The mixed melting point showed no depression on admixture with an authentic specimen obtained by the partial reduction of the t-A-t isomer VII. Also, the ultraviolet spectra of these two samples were found to be identical.

trans, trans-p-Phenylethynyl-p'-styrylstilbene (t-t-A) (XXI) and trans, cis-p-Phenylethynyl-p'-styrylstilbene (t-c-A) (XXII).—To a mixture of p-tolaldehyde (XX, 1.0 g., 4.9 mmol.) and finely powdered phosphonium salt (XI, 3.0 g., 5.6 mmol.) was added an excess of lithium ethoxide in absolute ethanol. After 30 min., the mixture was heated to 50~60°C for 2 hr. The solid deposited on cooling the reaction mixture was filtered and washed with ethanol. This was crystallized from chlorobenzene, yielding t-t-A (XXI), in the form of light greenish yellow plates, m. p. 308~309°C, 0.76 g. (40.6%).

Found: C, 94.25; H, 5.95. Calcd. for $C_{30}H_{22}$: C, 94.20; H, 5.80%.

The filtrate was concentrated to dryness under reduced pressure. The residual solid was dissolved in benzene and chromatographed over alumina in a dark place. The first fraction, eluted with benzene, gave t-c-A (XXII), in the form of light yellow plates, m. p. 198~199°C, 0.56 g. (29.9%). An analytical sample, melted at the same temperature, was obtained on recrystallization from benzene.

Found: C, 94.38; H, 5.91. Calcd. for $C_{30}H_{20}$: C, 94.20; H, 5.80%.

This substance isomerized to the t-t-A isomer XXI at its melting point. Also, the photoisomerization of XXII to XXI was confirmed by the observation of the ultraviolet spectrum of XXII on an insolation of the solution.

trans, trans, cis-p, p'-Distyrylstilbene (t-t-c) (XVIII).—a) From t-t-A (XXI) by Partial Reduction.—The solubility of XXI in tetrahydrofuran was found to be 1 mg./9 ml. The hydrogenation was carried out in the same manner as described in the case of t-A-t isomer VII. The benzene solution of the reduction product was chromatographed over alumina and eluted with the same solvent. The crystals of m. p. ca. 227°C obtained from the eluate was recrystallized from benzene, resulting in XVIII, in the form of light yellow prisms, m. p. 226~229°C. The mixed melting point determination proved the identity of this substance with the specimen obtained by method b).

b) From p-Styryl-[p'-formylstyryl]benzene (XVI) by the Wittig Reaction.—p-Styryl-[p'-methylstyryl]benzene (XIV).—An excess of lithium ethoxide in ethanol (0.2 g. of lithium and 130 ml. of absolute ethanol) was stirred into a mixture of p-tolaldehyde¹⁴ (XIII, 2.8 g., 0.022 mol.), powdered phosphonium salt (XI, 11 g., 0.021 mol.) and absolute ethanol (130 ml.), and the mixture was refluxed gently for 5 hr. The crystals deposited from the cooled reaction mixture were filtered, yielding crude

XIV. The second crop of XIV was obtained from the filtrate on exposure to sunlight to convert the cis-isomer to the trans compound. The combined crude XIV was washed with ethanol and recrystallized from chlorobenzene, yielding light yellow plates with a green fluorescence, m. p. 264~265°C, 1.8 g. (29.6%).

p-Styryl-[p'-formylstyryl]benzene (XVI).—A mixture of XIV (2 g., 6.7 mmol.) and N-bromosuccinimide (1.4 g., 7.8 mmol.) in chloroform (200 ml.) was refluxed for 8 hr. in the presence of benzoyl peroxide (200 mg.). After cooling the reaction mixture (a deposition of crystalline mass was observed), hexamethylenetetramine (3.5 g., 0.025 mol.) in chloroform (35 ml.) was added and the mixture was refluxed for 4 hr. The amine complex deposited on cooling the reaction mixture was filtered and mixed with aqueous acetic acid (160 ml.). The mixture was refluxed for 2 hr. to hydrolyze the complex. The crystals deposited from the cooled reaction mixture were washed with a small amount of ethanol and recrystallized from chlorobenzene, resulting in XVI, in the form of yellow thin plates, m. p. 250~253°C.

Found: C, 88.63; H, 5.84. Calcd. for $C_{23}H_{18}O$: C, 88.99; H, 5.84%.

UV_{max}(mμ) 242 (ε=20000), 273 (61400) (in dioxane).

IR_{max}(cm⁻¹) 1702, 1166 (-CHO).

t-t-c (XVIII) and t-t-t (IV).—A solution of the above-mentioned aldehyde (XVI, 370 mg.) in dry tetrahydrofuran (250 ml.) was mixed with benzyl-triphenylphosphonium chloride (XVII, 650 mg.) in ethanol (40 ml.). A small excess of lithium ethoxide in ethanol (15 ml.) was stirred drop by drop into the mixture at room temperature. Then, the mixture was heated at 40~50°C for 8 hr. while continually being stirred. The crystals deposited from the cooled reaction mixture were filtered and identified as all-trans isomer IV by means of a mixed melting point determination. The residue obtained on concentrating the filtrate under reduced pressure was dissolved in benzene and chromatographed over alumina. The fractions 3~5, eluted with benzene, gave crystals of m. p. 224~226°C*. The fractions 3~7, eluted with benzene, resulted in crystals of m. p. 224~228°C*. This was recrystallized carefully from benzene to give XVIII, in the form of light yellow prisms, m. p. 227~230°C*.

Found: C, 93.57; H, 6.46. Calcd. for $C_{30}H_{24}$: C, 93.71; H, 6.29%.

trans- and cis-Bis(p-phenylethynyl)stilbenes (A-t-A, XXV and A-c-A, XXVI).—p-Phenylethynyl-benzyl-triphenylphosphonium Bromide (XXIV).—A mixture of p-methyltolan¹⁴ (7 g., 0.031 mol.), N-bromosuccinimide (7 g., 0.039 mol.) and benzoyl peroxide (200 mg.) in carbon tetrachloride (80 ml.) was stirred under reflux for 6~7 hr. The succinimide deposited on cooling was removed. The oily material admixed with crystals was obtained by

* The t-t-c isomer was found to be thermally unstable. The melting point was determined by a rapid elevation of the temperature of the heating bath to avoid a rearrangement to all-trans isomer; otherwise the t-t-c isomer showed the melting point of the t-t-t isomer.

¹⁴ G. Drefahl and G. Plötner, *Chem. Ber.*, **93**, 990 (1960).

concentration of the filtrate and dissolved in benzene. The solution was passed through a short column of alumina and the solvent removed in vacuo. To a toluene solution of the residue was added triphenylphosphine (8 g., 0.031 mol.). The mixture was refluxed for 7 hr. under stirring. The solid deposited from the cooled reaction mixture was washed three times with ethanol, yielding XXIV, a colorless amorphous solid, m. p. 286~288°C, 7.0 g. (36%).

A-t-A (XXV) and A-c-A (XXVI).—A small excess of lithium ethoxide in absolute ethanol (80 ml.) was added dropwise to a suspension of the phosphonium salt (XXIV, 3.0 g., 5.6 mmol.) and tolanaldehyde^{1,12} (XX, 1.0 g., 4.8 mmol.) in absolute ethanol (150 ml.) at room temperature, and the mixture was stirred for 20 hr. The crude crystals deposited from the reaction mixture were digested with hot benzene and filtered (Filtrate A). The insoluble crystalline mass was recrystallized twice from chlorobenzene, yielding XXV, in the form of light yellow needles with a green fluorescence, m. p. 278~279°C, 0.30 g. (16.5%).

Found: C, 94.25; H, 5.32. Calcd. for $C_{30}H_{20}$: C, 94.70; H, 5.30%.

The filtrate A was chromatographed over alumina. The fractions 1 and 2, eluted with benzene, gave crystals of m. p. 149~151°C. This was recrystallized from ethanol-benzene (9:1) to give XXVI, in the form of colorless plates, m. p. 151~152°C, 0.34 g. (18.7%).

Found: C, 94.61; H, 5.31. Calcd. for $C_{30}H_{20}$: C, 94.70; H, 5.30%.

The ultraviolet spectrum of XXVI changed to that of XXV on the insolation of the solution.

The total yield of the Wittig reaction was found to be 0.46 g. (35%).

cis,trans,cis-, trans,trans,trans- and trans,trans,cis-p,p'-Distyrylstilbenes (XXVIII, IV and XVIII).—*p,p'-Stilbenedialdehyde (XXVII).*—The dialdehyde (XXVII) was prepared according to the usual method. The crude dibromide obtained by the reaction of *p,p'*-dimethylstilbene with *N*-bromosuccinimide was converted without purification to XXIX by the Sommelet reaction. The product was recrystallized from acetic acid to give pure XXVII, in the form of long yellow needles, m. p. 170~171°C, 3.5 g. (19.3%) (lit. value¹⁴, 169~170°C, 8% yield).

Found: C, 80.95; H, 5.16. Calcd. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12%.

c-t-c (XXVIII), t-t-t (IV) and t-t-c (XVIII).—To the stirred suspension of benzyltriphenylphosphonium chloride (XVII, 3.6 g., 9.3 mmol.) in absolute alcohol (30 ml.) was added excess of lithium ethoxide (from 0.2 g. of lithium) in absolute alcohol (40 ml.). After stirring for 1 hr., tetrahydrofuran (30 ml.) was added and stirred for 30 min. To the stirred mixture was added dropwise stilbenedialdehyde (XXVII, 1.0 g., 4.2 mmol.) in tetrahydrofuran (80 ml.) and absolute alcohol (10 ml.). The mixture was stirred for 2 hr. at room temperature and 8 hr. at 40~50°C. After cooling, the crystals deposited were filtered, and the filtrate was diluted with water (ca. 1 l.), precipitating the crystals. The combined crystals were dried, extracted with hot benzene and filtered. The cooled filtrate was filtered to remove the crystals A deposited and chromatographed over alumina in a dark place. Fractions 2 and 3, eluted with benzene, afforded XXVIII, m. p. 109~111°C, which was recrystallized from alcohol to give greenish yellow plates with a green fluorescence, m. p. 111~112°C, 0.18 g. (11%).

Found: C, 93.71; H, 6.27. Calcd. for $C_{30}H_{24}$: C, 93.71; H, 6.29%.

This substance, thermally more stable than *t-c-t* and *t-t-c*, isomerized to *t-t-t* isomer at 170°C and photoisomerized to *t-t-t* on the insolation of the solution.

Fractions 4~6, m. p. 224~228°C, were recrystallized from benzene, yielding light yellow prisms with a green fluorescence 2.0 g. (12%), and were found to be identical with *t-t-c* (XVIII) by the determination of the ultraviolet spectrum and the mixed melting point.

The insoluble crystals, m. p. 310~320°C, 0.15 g. (9%), in hot benzene, showed an identical ultraviolet spectrum with *t-t-t* (IV) and the crystals A were found to be a mixture of *t-t-c* and the recovered aldehyde (XXVII).

The cost of this research was partly defrayed by the Scientific Research Expenditure Fund of the Ministry of Education, to which authors' thanks are due.

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